

# Study of early-age hydration of Calcium Aluminate Cements through Transmission X-ray Microscopy

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## INTRODUCTION

Modern construction requires advanced concretes that have high strength, cost effectiveness and durability. Calcium Aluminate Cement concretes provide unique properties such as rapid strength development, high temperature resistance, and resistance to a wide range of chemically aggressive conditions. They are typically the material of choice for the refractory industries, pipes and sewer constructions, industrial floors, dam spillways, cold concreting and repair constructions in general.

Fresh concrete is prepared by mixing cement, aggregates and water. During at least four hours, there should be an induction period of the chemical reactions in order to allow the fresh concrete to flow into the formwork. The liquid suspension transforms then into a solid hardening material due to the relatively fast hydration of cement particles (setting process). Currently, there is little information on the induction period and on the formation of the primary hydrates. Scrivener and Capmas [1] showed that early amorphous hydrates could precipitate in Calcium Aluminate Cements before the setting time and reduce the workability of the fresh concrete. In addition, they may control the setting time of the cement by inhibiting further hydration of cements grains. Two theories have been advanced to explain the induction period: the primary hydrates may coat the cement grains and form a protective barrier to further dissolution (diffusion rate control reaction) [2] or they may inhibit the nucleation of the main hydrates by changing the composition of the supersaturated solution [3]. It is clear that a better knowledge of these early amorphous hydrates can provide a clarification of the process of hydration during the first hours [4]. The primary hydrates have not been well characterized, because they are very sensitive to dried and vacuum environments necessary for conventional electron. The XM-1 microscope operated by the center for X-ray Optics on beamline 6.1.2 can provide new insight on the hydration process as sample can be observed wet, with high resolution, over time, as chemical reactions proceed. Improvements of workability and a better control of setting time of concrete can also be achieved through this technique.

## EXPERIMENTS

A cement paste made from distilled deionized water and pure monocalcium aluminate cement (CA with  $C=CaO$  and  $A=Al_2O_3$ ) with a mass water/cement ratio of 5 was placed in a wet chamber between two 120nm thick silicon nitride windows. The hydration of the cement grains at room temperature (22°C) was then followed continuously from the first minutes to the setting time by transmission X-ray microscopy at a wavelength of 2.4nm and at a magnification of 2400×.

## RESULTS

X-ray images show that a colloidal hydrate with a low density precipitates from the solution few minutes after mixing cement and water (Figure 1). The microstructure remains the same during one hour; after that another amorphous hydrate progressively covers the solid particles present in the solution (both cement grains and colloidal gel). This later hydrate looks like a membrane (Figure 2) but it is less stable than the early colloidal hydrate in the sense that some part of it dissolves and reprecipitates alternately. In addition, it is remarkable that even with the presence of these voluminous amorphous hydrates, the cement paste is still a workable liquid suspension since no significant hydration has occurred yet. Eventually, the massive nucleation of hydrates will end this induction period after around 8 hours of hydration (around 5 hours for commercial cements). The environmental XM-1 microscope allowed us to follow this event in situ and without any artifacts as shown from

Figure 2 to Figure 3. We can observe that the crystallization takes place in the solution and that the nucleation sites are homogeneously distributed inferring that the solution reached the saturation level everywhere at the same time. Furthermore, we observe that the early amorphous hydrates didn't transform during that massive nucleation process.

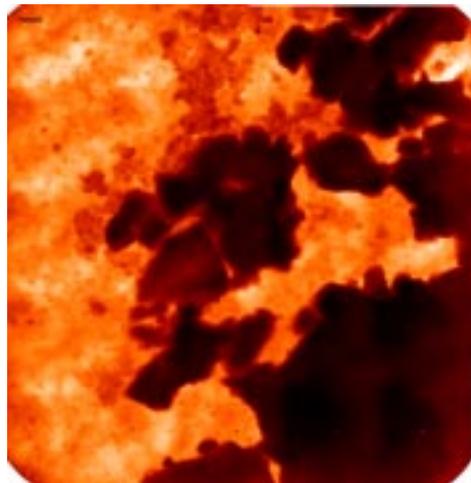


Figure 1: Tiled X-ray images of CA cement hydrated for 45 min. at  $w/c=5$ , 516.6eV, 1 sec. exposure time, scale bar=1\_m



Figure 2: Tiled X-ray images of CA cement hydrated for 7h35min. at  $w/c=5$ , 516.6eV, 1 sec. exposure time, scale bars 1\_m

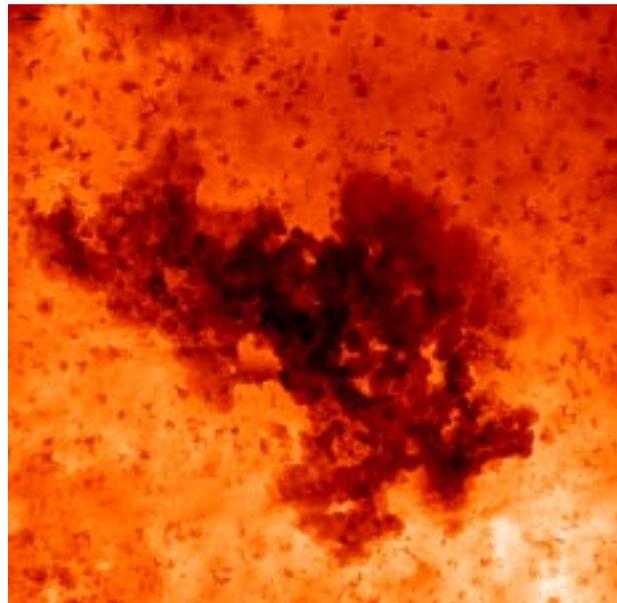


Figure 3: Tiled X-ray images of CA cement hydrated for 8h45min. at  $w/c=5$ , 516.6eV, 1 sec. exposure time, scale bar=1\_m

Near-edge X-ray absorption has also provided interesting information about the chemical composition of these two primary hydrates. By comparing images of the same spot (Figure 4) taken around the maximum absorption peak measured for calcium fluoride (349eV), we can map the concentration of calcium in the cement paste.

From the Figure 5, we observe that the colloidal gel contains less calcium than the membrane hydrate and the solution. Because we have only calcium and aluminum and in the same proportion in the cement paste, the colloidal gel should be relatively rich in aluminum.



Figure 4: Zoom on colloidal gel and membrane from Figure 2, 516.6eV, scale bar 1\_μm.

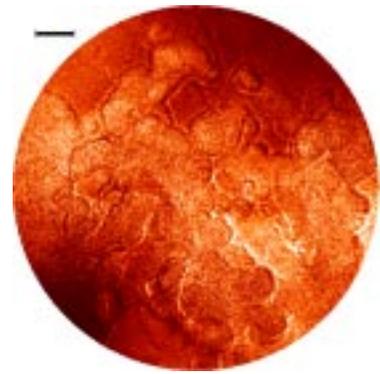


Figure 5: Same spot by dividing the image taken at 347eV by the one taken at 349eV. The dark areas have a relatively high calcium concentration

## CONCLUSION

This study has shown how X-ray microscopy can provide useful information on the hydration reactions of cements. This technique allowed us to identify two distinct primary amorphous hydrates that precipitate within the first hour in a Calcium Aluminate Cement paste: an aluminum-rich colloidal gel and a thin membrane. It is clear from their morphology that they can reduce the workability of the fresh concrete if they percolate in the solution.

For the first time in the cement chemistry, we have also been able to observe the massive nucleation process corresponding to the beginning of the setting process of a cement paste. The homogenized crystallization occurring in the solution without any change of the amorphous hydrates tends to reinforce the theory considering the early amorphous hydrates as a delaying agent of nucleation rather than a physical barrier to further dissolution. The effect of temperature on these amorphous hydrates and on the setting time of the cement paste is under investigation at the XM-1 microscope.

## REFERENCES

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